

Analysis of recycled PET bottles with Raman spectroscopy

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Introduction

Poly(ethylene terephthalate), or PET, is a synthetic polymer produced from oil and natural gas. It can be recycled either chemically or mechanically, making it 100% recyclable. This means that PET can be repeatedly processed into valuable products without losing its fundamental properties.

Today, many companies have pivoted to 100% recycled PET (R-PET) due to the environmental benefits of recycled materials. Bottles made with 100% R-PET are very similar, both visually and functionally, to those made with virgin PET (V-PET). Most bottles made with 100% R-PET are, at this time, the result of a single recycling cycle, but the environmental benefits could increase proportionately with each additional cycle.

Current EU legislation dictates that manufacturers will have to utilize bottles made with a minimum amount of R-PET by specific thresholds: $\geq 25\%$ R-PET by 2025 and $\geq 30\%$ R-PET by 2030.¹ However, there is currently no consolidated technique available to evaluate a material for the percentage of R-PET that it contains in combination with V-PET. In this application note, a fast, easy, and robust method for the classification of R-PET percentage is proposed utilizing Raman spectroscopy.

Raman spectroscopy has long been utilized to investigate the structure of polymers, including their molecular conformation, orientation, and crystal structure. It can be combined with multivariate analyses, such as discriminant analysis, to correlate statistically observed spectral variations with known sample properties such as crystallinity and density to determine the amount of recycled material in virgin samples.

¹ Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 (<https://eur-lex.europa.eu/eli/dir/2019/904/oj>)

Methods

Clear bottle preforms containing mixtures of virgin and recycled PET were either purchased on the market or prepared by Sacmi specifically for this project by combining V-PET pellets and R-PET flakes.

Preforms were analyzed as received, without any sample preparation. Raman spectra were recorded at the neck area from the outside surface, as this region remains unstretched during bottle molding, leaving polymer crystallinity and chain alignment unaffected.

Post-consumer R-PET samples were supplied by ILPA-MP3 in the form of flakes and by Aliplast as pellets. V-PET with IV = 0.84 dl/g was purchased commercially under the tradename RAMAPET R1 (Indorama Ventures, Singapore).

A different set of samples were prepared by melt mixing V-PET and R-PET. Pellets and flakes were first dried under vacuum at 120°C overnight and then combined in a Brabender Plasticorder PL2000 equipped with a 50 EHT electrically heated mixer. To ensure uniform mixing, pellets and flakes were mixed at 260°C for 5 min and then cooled at room temperature. Samples were prepared to cover the full range from 0–100% R-PET by weight at 10% increments. To facilitate Raman analysis, specimens were then prepared by compression molding in a custom-made laboratory mold. Pure V-PET and R-PET specimens were also molded under the same conditions. For each composition, three specimens were analyzed, and Raman spectra were recorded at three different locations in order to minimize the effect of any potential contamination and/or inhomogeneity in the R-PET.

Raman spectra were recorded using the Thermo Scientific™ DXR3 Raman Microscope and the Thermo Scientific™ DXR3 Flex Raman Spectrometer, equipped with a 780 nm and 785 nm laser, respectively.

Exposure time, number of exposures, and laser power were adjusted to record high-quality spectra with a high signal-to-noise ratio (SNR).



Figure 1. DXR3 Raman Microscope and DXR3 Flex Raman Spectrometer.

Results

Measured spectra for all samples were largely similar, with a few differences in the region between 1,500 and 1,100 cm^{-1} , resulting from the absorption of C-H aromatics and aliphatic bending.

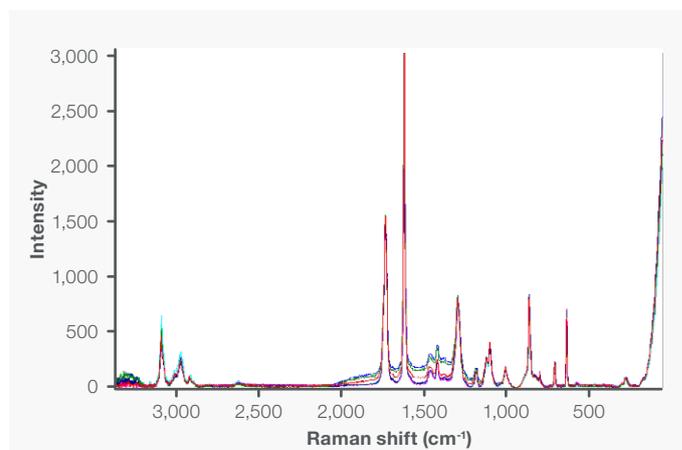


Figure 2. Raman spectra of several samples with varying ratios of virgin and recycled PET. (R-PET content ranging from 0% to 100% by weight.)

Using the discriminant analysis algorithm in Thermo Scientific™ TQ Analyst™ Software, it was possible to classify the samples as a function of their R-PET percent by weight.

Discriminant analysis

Discriminant analysis can be used to determine the class or classes of known material(s) that are most similar to an unknown by computing its distance from each class center in Mahalanobis distance units. This technique is typically used to screen if incoming materials are one of three known compounds (a, b, or c).

Discriminant analysis methods typically specify at least two classes of known materials, but the method also works with only one class. Multiple standards may be used to describe each class (at least one class must contain two or more standards). Multiple regions of the spectrum may be used for the analysis.

The algorithm can be used to screen a variety of samples against a known material, or it can be used to calculate the Mahalanobis distance between an unknown sample spectrum and a set of standards.

In this application note, the spectral information in the specified region(s) of an unknown sample spectrum is compared to a stored calibration model to determine which class of standards is most similar to the unknown.

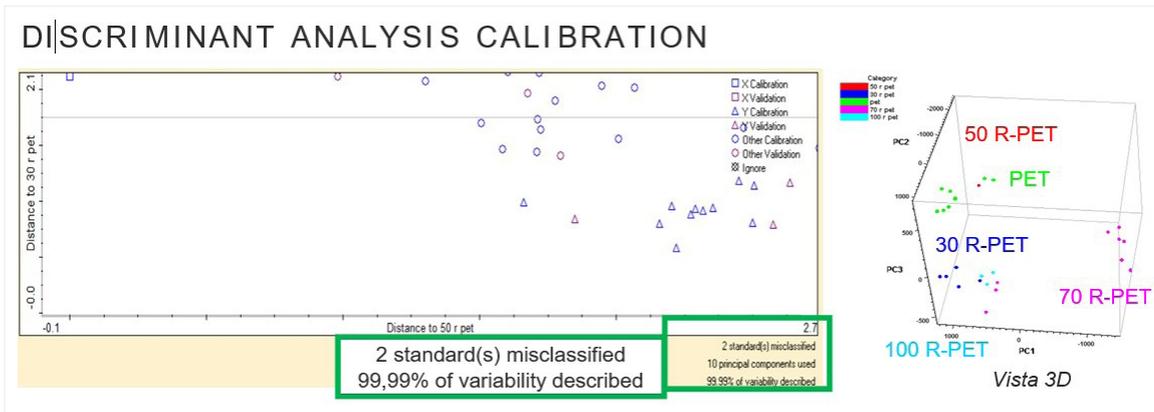


Figure 3. Discriminant analysis calibration and 3D plot of standards with different R-PET content, plotted according to the first three principal components.

During calibration, the software computes a mean spectrum and then generates a distribution model by estimating the variance at each frequency in the analysis range. You can select whether a unique distribution model is developed for each class or one model is used for all classes. If one model is used for all classes, the software subtracts the class average from each standard and then creates a single variance spectrum using information from all of the classes. If you elect to use a unique distribution model for each class, the software subtracts the class average from each standard and uses only the information from a given class to create a unique variance spectrum. This is similar to the technique known as SIMCA (soft independent modeling of class analogies).

In order to calculate the statistics properly, the single model requires at least one class that contains two or more standards. If you select the option that creates a unique distribution model for each class, every class must contain at least two standards.

When this method is used to analyze an unknown sample, the software performs a principal component analysis on the spectra of the standards and uses those results to determine score values for the unknown sample spectrum. The score plots are used to produce Mahalanobis distance values, which in turn are used to rank the classes.

The final output of the discriminant analysis is the name(s) of the class or classes that are most similar to the spectrum of the unknown sample. The Mahalanobis distance between the unknown sample and each class can also be reported. The closer each distance value is to zero, the better the match.

Analysis

Discriminant analysis proved to be an effective method for classifying the different amounts of R-PET in the samples. A large number of standards were analyzed to further improve this capability. Those standards ranged from bottle preforms, to bottles ready to be filled, to plaques that were compression molded in a lab. This procedure was put in place to decouple the results of the analytical method from the origin of the standard specimens.

Generally, samples from bottles and preforms produced expected results. Bottles with different spectra and incorrect classification (i.e., Mahalanobis distances that are too high) likely contained variable pigment content, a consequence of different colored bottles being used to produce the R-PETs. In future, it would be necessary to include colored bottles during the calibration phase to account for this.

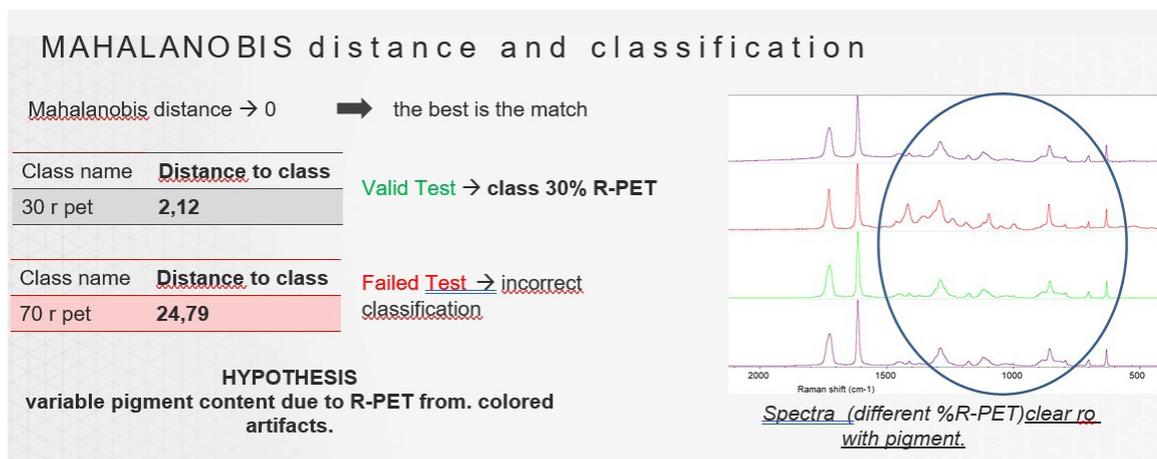


Figure 4. Examples of valid and failed classifications for R-PET samples.

The interim solution was to create a library of spectra collected from bottles with different degrees of R-PET and slight coloring. This way, before real samples were analyzed, it could be verified if the unknown sample contains any pigmentation.

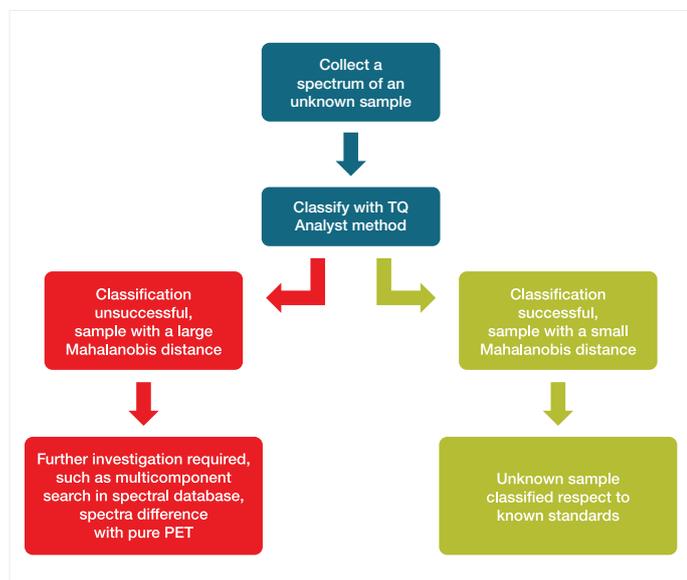


Figure 5. Classification workflow.

Conclusions

Through a combination of Raman spectroscopy and discriminant analysis classification, the presence of recycled PET within virgin PET can be determined in a few seconds without any sample preparation. Further refinement of the technique would benefit from the inclusion of colored PET samples in the calibration, to account for the presence of pigments in R-PET source materials.

Acknowledgments

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